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THEORETICAL STUDY OF CYCLOPROPANE AND CYCLOPROPYL RADICAL: STRUCTURE AND VIBRATIONAL ANALYSIS

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THEORETICAL STUDY OF CYCLOPROPANE AND CYCLOPROPYL RADICAL: STRUCTURE AND VIBRATIONAL ANALYSIS

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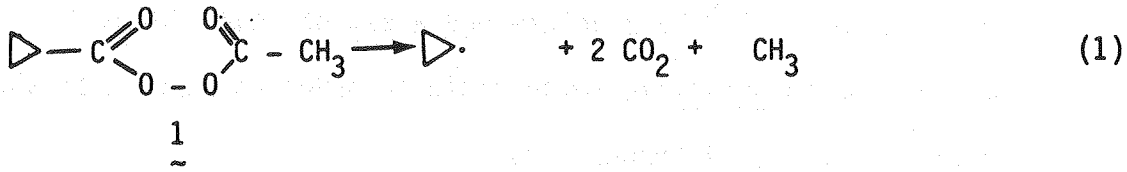
Abstract

Ab initio Hartree-Fock calculations of the structure and vibrational frequencies of cyclopropane and cyclopropyl radical are presented. It is found that the αCH bond in the radical is bent 39.3^{o} out of the CCC plane, the inversion barrier is 3.0 kcal/mole and the pyramidal bending mode has a frequency of 713 cm^{-1}. Compared to cyclopropane, the αCC bonds are stronger, and the βCC bond is weaker in the radical. The shortening of the αCH bond, and the hyperconjugative interaction of the unpaired electron onto the βCH bonds previously observed in alkyl radicals, are found to be much less pronounced in cyclopropyl radical.

I. Introduction

Previously[1,2] we have used ab initio Hartree-Fock (HF) calculations to aid in the determination of the structure and normal coordinate analysis of alkyl radicals. A consistent analysis of the structures and dynamics of alkyl radicals was obtained from the calculations and the infrared spectra generated in low temperature matrices.[3] It resulted in a complete assignment of all the bands of the alkyl radical.[4] Here we report HF calculations on the smaller cyclic radical, the cyclopropyl radical.

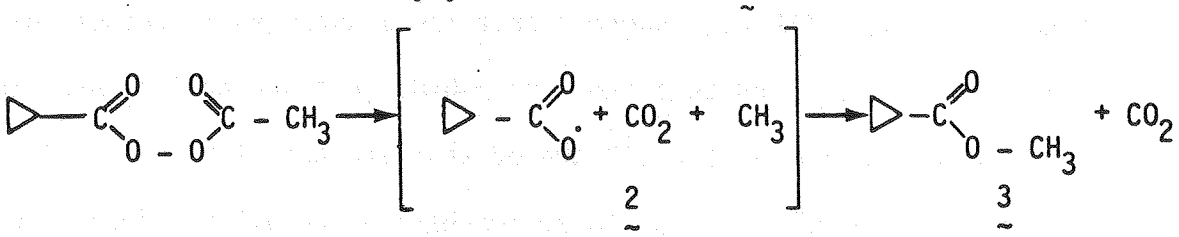
Experimentally the isolation of the cyclopropyl radical in rare gas matrices has proven to be difficult. Indeed it has a high chemical reactivity for hydrogen atom abstraction, and it is difficult to prepare by a thermal bond fission reaction because of its unfavorable heat of formation. Photolysis of acetyl cyclopropyl peroxide 1 isolated in an argon matrix was attempted with the expectation to form cyclopropyl radical as shown below:



(1)

1

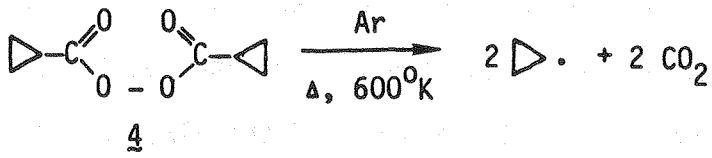
Instead the reaction only yielded the ester 3 as indicated below:



(2)

2 3

Presumably the acyloxy radical 2 has a long lifetime and instead of decarboxylating, combines with the methyl radical to form the ester. Flash vacuum pyrolysis experiments[5] were performed on the diacyl peroxide 4 mixed in argon gas as indicated in Eq. (3):



4 (3)

By rapidly condensing the gaseous products emerging from the pyrolysis tube the radicals may be stabilized and observed spectroscopically. However, although the radicals are successfully produced the spectroscopic observation is ambiguous because of the presence of another radical species, most likely the allyl radical resulting from thermal conversion of cyclopropyl radical.[6]

The cyclopropane molecule has been extensively studied both experimentally and theoretically. A detailed description of the force field and assignment of the infrared spectra has been reported by Duncan et al.[7] Blom et al.[8] have determined a set of scale factors to be applied on an ab initio force field in order to reproduced the experimental vibrational frequencies.

The cyclopropyl radical has been observed by electron spin resonance (ESR) methods.[9] ESR data suggest that the α-hydrogen is out of the plane of the ring, and that the four β-hydrogens are equivalent. INDO calculations by Kochi et al.[10] showed that the out of plane angle for the αCH bond is 35°, with an inversion barrier of 3.2 kcal/mole. Furthermore the calculated coupling constants for the syn and anti β-hydrogens

are nearly equal to each other for all values of the bending angle, indicating that rapid pyramidal inversion at the radical site is not necessarily required to explain the apparent magnetic equivalency of the four βhydrogens.

In this paper we report HF ab initio calculations of the structures and vibrational spectra of cyclopropane and cyclopropyl radical. Section II describes the computational method used. Section III contains a detailed description of the structures of C_3H_8 and C_3H_7. The normal modes and vibrational frequencies are presented in section IV.

II. Computational Method

The calculated wavefunctions are of closed shell spin restricted HF[11] type for cyclopropane, and spin unrestricted UHF[12] type for cyclopropyl radical, using the standard "split valence" 4-31G basis.[13] In the UHF formalism the doublet spin state of cyclopropyl is contaminated with higher spin states. The amount of contamination is shown in the calculated value of the expectation of value of S^2. In all the calculations reported here, S^2 was found to be ~0.76, compared to the exact value of 0.75, indicating that the wavefunction is nearly a pure doublet.

The structures of the molecular species were determined by minimizing the energy with respect to all geometrical degrees of freedom simultaneously using the analytically calculated energy gradient. The force constant matrices, calculated at the respective equilibrium geometry, were obtained from numerical differences of the energy gradient as proposed by McIver et al.[14] The calculations were carried out with the computer code HONDO.[15]

III. STRUCTURES OF CYCLOPROPANE AND CYCLOPROPYL RADICALS

The D_{3h} conformation of cyclopropane is shown in Fig. 1. The calculated C-C bond length (1.501 Å), is shorter than the C-C single bond in ethane (1.529 Å with the 4-31G basis[16]). Similarly the computed CH bond length (1.071 Å) is shorter than the value in ethane (1.083Å). The corresponding experimental values[17] are R(CC) = 1.510 Å and R(CH) = 1.089 Å. There is a widening of the HCH angle 113.9° above the tetrahedral values (experimentally <(HCH) = 115.1°).

The optimized structure of the cyclopropyl radical with C_s symmetry is shown in Fig. 2. The most important features of the structure are:

i) The radical center is nonplanar with γ, the angle between the αCH bond and the ring, equal to 39.3°. The βCH bonds form an angle of 56.8° with the plane of the ring, very close to the corresponding value in cyclopropane (57.0°). The structure corresponding to a planar radical center has C_{2v} symmetry, and represents the transition state in the inversion motion of the radical center. The energy of the fully opti-

Figure 3. [illegible] bending potential for [illegible]

solid line corresponds to geometries where all the bond lengths and bond angles have the value obtained for the C_s symmetry lowest energy structure, except for the bending angle γ. The dotted line represents an interpolated energy curve connecting the C_s and C_{2v} structures. Point A is the stable conformation of C_s symmetry, point B is the lowest energy C_{2v} symmetry structure and is 3.0 kcal/mole above A, point C is the structure with parameters identical to point A, except for the γ angle set at 0.0°. Point C is only 0.19 kcal/mole above B.

ii) The αCH bond is 1.067 Å long. It is shorter than the CH bonds in cyclopropane (1.071 Å). The bond shortening is in qualitative agreement with the effects observed for acyclic alkyl radicals.[1] However, the shortening in this case is much less pronounced (CH = 1.086 Å in C_2H_6, αCH = 1.076 Å in C_2H_5). In acyclic alkyl radicals the αCH bond shortening resulted in very characteristically high frequency CH stretching bonds. For cyclopropyl the change in stretching frequencies is not expected to be as dramatic.

iii) The CC bonds are no longer all equivalent. The αCC bond lengths are 1.476 Å which is shorter than the CC bonds in cyclopropane (1.501 Å). The βCC bond length is 1.54 Å, longer than in C_3H_8. This is a clear manifestation of the presence of the unpaired electron. Thus the αCC bonds are stronger, and the βCC bond weaker than in cyclopropane. This result is in qualitative agreement with the known conversion of cyclopropyl radical to allyl radical by βCC bond breaking.[6]

iv) The βCH bonds are slightly longer than CH bonds in cyclopropane. A more pronounced lengthening effect was calculated for the acyclic alkyl radicals,[1] and attributed to hyperconjugative interaction. In addition, it is seen that there is almost no difference between the <u>syn</u> and <u>anti</u> βCH bonds.

v) Mulliken population analyses of the wavefunctions of cyclopropane and the cyclopropyl radical are given in Table 1. In cyclopropane each hydrogen contributes 0.17 electrons to the carbon it is attached to. In the cyclopropyl radical the α-hydrogen contributes the same amount. However, out of the 0.17 electrons donated by the α-hydrogen, only 0.12 goes

Table 1. Mulliken population analyses for cyclopropane C_3H_8 (D_{3h} symmetry) and cyclopropyl radical C_3H_7 (C_s symmetry).[a]

		Cyclopropane	Cyclopropyl
C_o	s	3.31	3.32
	p	3.04	2.80
	total	6.35	6.12
H_o	s	0.83	0.83
C_1	s	—	3.33
	p	—	3.05
	total	—	6.38
H_1	s	—	0.82
H_2	s	—	0.82

[a]See Figures 1 and 2 for labels.

to the carbon radical center, and 0.05 goes to the β-carbons which then carry 0.22 electrons more than the radical center. Again we note that the syn and anti hydrogens of the radical carry the same electronic charge. Therefore, on the basis of bond lengths and electronic charges, we conclude that the β-hydrogens are nearly equivalent to each other.

IV. THEORETICAL VIBRATIONAL ANALYSIS OF CYCLOPROPANE AND CYCLOPROPYL RADICAL

Previous studies[18,19] have shown that although the calculated values are higher than the observed frequencies, they appear in the correct order. Exceptions to this usually occur when the vibrational frequencies are closely spaced. When these situations arise it is difficult to make a meaningful comparison between the theoretical and experimental results because the theoretical values are harmonic vibrational frequencies while the experimental values are usually the observed frequencies uncorrected for anharmonicity. In spite of this, the theoretically determined frequencies are a valuable aid for assigning vibrational spectra.

The calculated and observed vibrational frequencies for cyclopropane (Table 2) are listed in order of decreasing frequency. The CH stretches are found at 3300-3400 cm^{-1} (expt. 3000-3100 cm^{-1}); the CH_2 bends at ~1650 cm^{-1} (expt. 1450 cm^{-1}); CH_2 rocks, twists and wags are intermixed between 1200 and 1350 cm^{-1} (expt. 1000-1200 cm^{-1}). Because of the small differences in frequencies between some of these modes, the ordering is somewhat different for the calculated frequencies. The symmetric CCC stretch is found at 1288 cm^{-1} (expt. 1188 cm^{-1}), and the asymmetric one at 950 cm^{-1} (expt. 869 cm^{-1}). The two lowest frequency modes are a CH_2 rock at 941 cm^{-1} (expt. 854 cm^{-1}), and a CH_2 twist at 848 cm^{-1} (expt. 738 cm^{-1}).

Table 2. Vibrational frequencies of cyclopropane C_3H_8 (D_{3h} symmetry).

Symmetry	Mode		ν(obs. cm^{-1})	ν(calc. cm^{-1})
A''_2	CH	stretch	3102	3414
E"	CH	stretch	3083	3389
A'_1	CH	stretch	3038	3327
E'	CH	stretch	3024	3312
A'_1	CH_2	bend	1482	1673
E'	CH_2	bend	1438	1635
E"	CH_2	rock	1187	1347
A'_2	CH_2	wag	1070	1292
A'_1	CCC	sym. stretch	1188	1288
A''_1	CH_2	twist	1126	1277
E'	CH_2	wag	1028	1226
E'	CCC	asym. stretch	869	950
A''_2	CH_2	rock	854	941
E"	CH_2	twist	738	848

In spite of the numerical differences between the experimental and theoretical frequencies in cyclopropane, a comparison of the theoretical data for cyclopropane and cyclopropyl radical should reveal the structural differences between the two species. The calculated frequencies for cyclopropyl radical are given in Table 3. The radical has C_s symmetry, lower than D_{3h} of cyclopropane, resulting in removal of irreducible representation degeneracies. The range of CH stretch frequencies is 3286-3418 cm^{-1} (3312-3414 cm^{-1} in cyclopropane). The αCH stretch is higher than any of the stretches involving the βCH bonds in accord with the small bond shortening of αCH. However the differences in stretching frequencies between C_3H_8 and C_3H_7 induced by the radical center are much less noticeable than in the ethyl radical[1] where the αCH bonds acquire a strong ethylenic character. The αCH stretches in the ethyl radical are readily identifiable both experimentally and theoretically. For the cyclopropyl radical no such obvious shift is predicted. The CH_2 bends are found at ~1630 cm^{-1} (barely lower than in C_3H_8). The symmetric breathing CCC stretch is at 1314 cm^{-1}, slightly higher than in C_3H_8 (1238 cm^{-1}) indicating somewhat stronger αCC bonds. The asymmetric αCC stretches and the βCC stretch originate from the asymmetric degenerate CCC deformation mode of cyclopropane (950 cm^{-1}). The αCC asymmetric stretch is at 995 cm^{-1}, and the βCC stretch is at 916 cm^{-1} indicative of the βCC bond weakening already apparent from the optimized geometry shown in Figs. 1 and 2. The 995-916 cm^{-1} splitting of CC stretches is clearly characteristic of the cyclopropyl radical. In the lower C_s symmetry of the radical the CH_2 twisting, rocking, and waging motions are no longer

Table 3. Vibrational frequencies of cyclopropyl radical C_3H_7 (C_s symmetry).

Symmetry	Mode		ν (calc. cm^{-1})
A'	αCH	stretch	3418
A'	βCH	stretch	3373
A"	βCH	stretch	3358
A'	βCH	stretch	3293
A"	βCH	stretch	3286
A'	CH_2	bend	1646
A"	CH_2	bend	1623
A'	CCC	sym. stretch	1314
A"	CH_2	asym. twist	1301
A"	CH_2	asym. wag	1268
A'	CH_2	sym. rock + αCH rock	1241
A"	αCH	wag	1208
A'	CH_2	sym. wag	1204
A"	αCC	asym. stretch	995
A'	βCC	sym. stretch	916
A"	CH_2	asym. rock + αCH wag	893
A'	CH_2	sym. twist	870
A'	αCH	sym. bend	713

pure, and contain some contamination from the motion of the αCH bond. This is most evident for the CH_2 rocking modes at 1241 and 893 cm^{-1} (1347 and 941 cm^{-1} in C_3H_8). Another characteristic mode is found at 713 cm^{-1}. This is the pyramidal bending mode of the radical center. Its frequency is lower than any of the cyclopropane frequencies. The bending angle of 39.3^{o} and the inversion barrier of 3.0 kcal/mole are indicative of this pyramidal type bending mode.

V. CONCLUSION

The theoretical calculation of the vibrational frequencies of the cyclopropyl radical reveals two characteristic features of its infrared spectrum:

i) The pyramidal type bending mode of the radical center corresponds to a frequency lower than any of the frequencies of cyclopropane, and is found at 713 cm^{-1}.

ii) The CCC asymmetric degenerate stretching mode at 950 cm^{-1} in cyclopropane splits into two stretching modes at 995 cm^{-1} and 916 cm^{-1} in the cyclopropyl radical. The 916 cm^{-1} mode corresponds to the βCC bond cleavage which leads to the formation of the allyl radical.

In addition it is found that no significant hyperconjugative interaction takes place between the radical center unpaired electron, and the βCH bonds, which are nearly equivalent to each other.

The theoretical vibrational analysis presented here is expected to help in the identification of the infrared spectrum of the cyclopropyl radical. Because of the ease of thermal conversion of cyclopropyl into allyl radical a theoretical study of the allyl radical similar to the one presented here should provide complementary information valuable for experimental studies on cyclic alkyl radicals. Such a study will be reported in a forthcoming publication.

ACKNOWLEDGMENT

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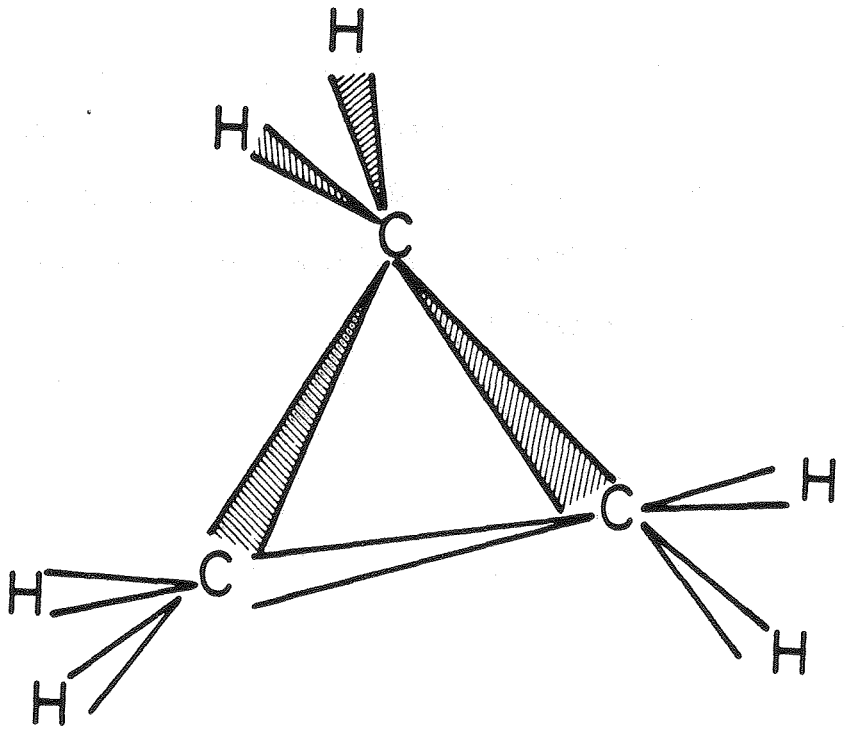

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Figure 1. HF equilibrium structure of cyclopropane[a] C_3H_8 (D_{3h} symmetry).

a. 4-31G basis. E = -116.883848 a.u.;
R(CC) = 1.501Å, R(CH) = 1.071Å,
< (CCC) = 60°, <(CCH) = 118.16°,
< (HCH) = 113.95°.

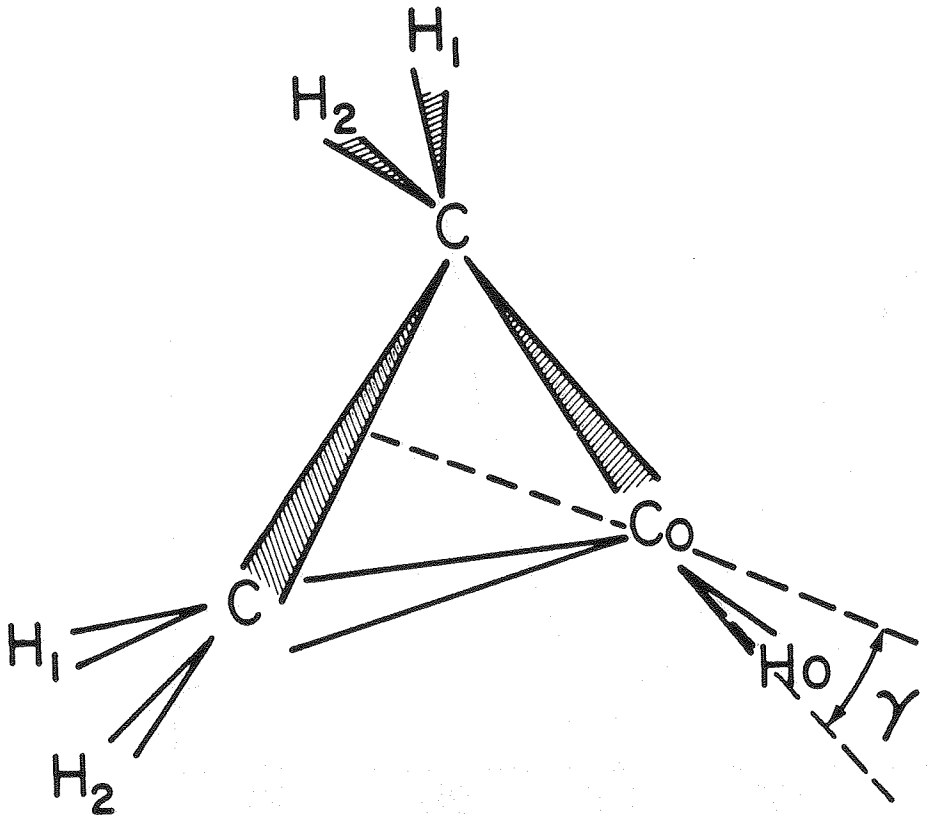

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Figure 2. HF equilibrium structure of the cyclopropyl radical[a] C_3H_7 (C_s symmetry).

a. 4-31G basis; E = -116.239404 a.u;
S^2 = 0.76; R(C_oC) = 1.476Å; R(CC) = 1.524Å;
R(C_oH_o) = 1.067Å; R(CH_1) = 1.073Å;
R(CH_2) = 1.073Å;
< (CC_oC) = 62.15°, < (CC_oH_o) = 131.51°,
< (C_oCH_1) = 119.16°, < (C_oCH_2) = 118.60°,
< (CCH_1) = 118.53°, < (CCH_2) = 117.59°,
< (H_1CH_2) = 113.59°, γ = 39.30°

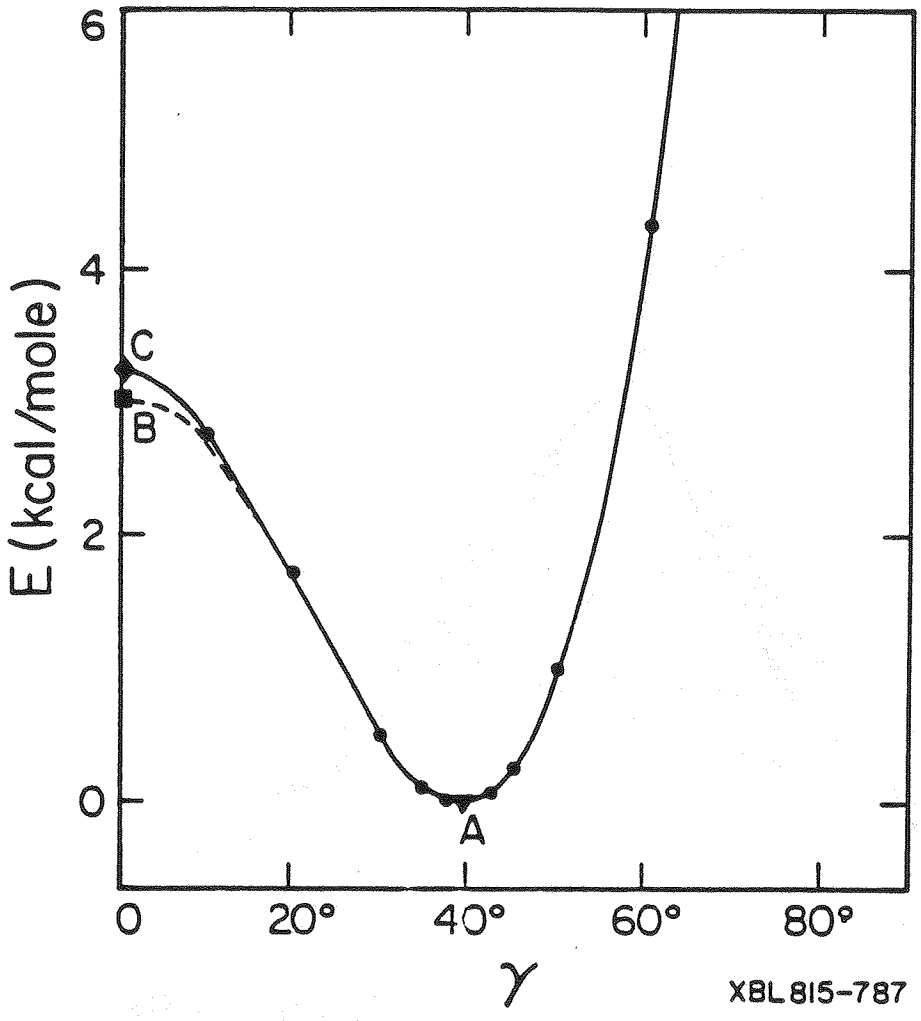

Figure 3. Bending potential for the motion of the α-hydrogen in the cyclopropyl radical.[a]

a. The dotted line is an interpolated curve which connects the C_s symmetry equilibrium conformation (point A) and the C_{2v} transition state conformation (point B) in the inversion motion of the radical center. For point C all the internal coordinates are the same as for point A except for the out-of-plane angle γ. The energies are:
point A, C_s symmetry, E = -116.239404 au;
point B, C_{2v} symmetry, E = -116.234572 au;
point C, C_s symmetry, E = -116.234262 au;